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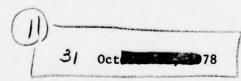   624-4354

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Pittsburgh Atomic Sciences Institute

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TECHNICAL PROGRESS REPORT NO. 25

Pittsburgh Atomic Sciences Institute

University of Pittsburgh

Pittsburgh, PA   15260

I. Summary of Research

This semi-annual progress report contains descriptions of the researches carried
out under contract N000-14-76-C-0098 during the period May 1978 to October 1978,
identifying the topics by title, senior investigator(s) in charge of the work, and the
general program to which they belong.

A. Laser Physics

1. Energy Transfer Processes of Laser Interest (F. Kaufman and E. C. Zipf)

a. F. Kaufman's Group

Excellent progress was made in our studies of vibrational relaxation of highly
excited HCl which are providing answers to a number of important and as yet unresolved
questions regarding the systematics of V – V, V – E, and V – R, T energy transfer pro-
cesses for small molecules containing 2 to 3 eV of vibrational energy. Our work on
$HCl^{\neq}$ is now almost completed and we will turn to HF and DF for which we have already
prepared the input parameters for our computer programs which first deconvolute the
measured, low-resolution IR chemiluminescence spectrum and then calculate relaxation
rate constants for added quencher species. The most interesting recent findings
pertain to the fate of transferred vibrational energy in off-resonance $HCl^{V} + HCl^{0}$
collisions as a guide to the relative importance of V – V vs. V – R, T processes.
(See section d.) Other results deal with further quencher efficiencies and with new
generating reactions.

<u>a</u>. Comparison of quenching by N_2 and CO. On the basis of energy resonance N_2 (2360 cm^{-1}) should relax HCl^v more rapidly than CO (2170 cm^{-1}), but the reverse is observed, presumably because of dipole-dipole interactions with CO. The rate constants for v = 4 to 7, in order k_{N_2}, k_{CO}, 10^{-13} cm^3 sec^{-1} are as follows: v = 4: 2.6, 23; v = 5: 3.5, 93; v = 6: 5.7, 200; v = 7: 3.9, 260; i.e. CO is 9 to 60 times more efficient than N_2. The magnitude of this effect and its increase with increasing v are surprisingly large.

<u>b</u>. Quenching by D_2. The large isotope effect brings the vibration frequency from 4395 cm^{-1} for H_2 to 3118 cm^{-1} for D_2. Relaxation of HCl^v by H_2 had earlier been found to be extremely slow, and so D_2 was tried since its frequency is fairly close to resonance with ground state HCl (2990 cm^{-1}) but goes increasingly off resonance for higher v ($\sim$100 cm^{-1} per $\Delta v = 1$). The quenching results bear this out nicely, i.e. the rate constants <u>decrease</u> for increasing v as follows in the order v = 1 to 7, in units of 10^{-13} cm^3 sec^{-1}: 1 - 10.2; 2 - 5.1; 3 - 4.6; 4 - 3.5; 5 - 2.2; 6 - 2.0; 7 - 1.6.

<u>c</u>. The number of generating reactions for HCl^v has been further increased for two reasons: (1) For some quencher species H-atom reactions cannot be used because of rapid, interferring H + quencher reactions (e.g. for NO_2); (2) Since rate information is always most accurate for the highest v-levels of any given initial distribution, it is important to be able to prepare widely differing such initial distributions.

Thus, we are using H + ICl and H + ClNO for the highest (7, 6, 5) vibrational states, Cl + HI and H + Cl_2 for lower states (4, 3), H + $SOCl_2$ (a new addition to our arsenal) for still lower states (3, 2), and Cl + HBr for v = 1 plus a very small amount of 2.

$\underline{d}$. The difficult and as yet almost totally unresolved question of the fate of the transferred vibrational energy in $HCl^V + HCl^O$ collisions is now being tackled experimentally. This involves careful measurements of the concentration of all v-states as increasing amounts of "cold" HCl are added, with particular emphasis on the increasing amounts of HCl(v = 1). The measured rate constants for HCl^V relaxation had earlier been found to rise from 3.3×10^{-12} for v = 2 to 4.5×10^{-11} cm^3 for v = 7. When interpreted as simple V - V shuffling reactions, e.g. $HCl^7 + HCl^0 \rightarrow HCl^6 + HCl^1$ this led to the surprising conclusion that the reverse reaction which is exothermic by 600 cm^{-1} would have to have a ca. 5 times gas kinetic rate constant. Our recent experiments in which we measure the buildup of HCl(v = 1) now tell us that high v-states (7, 6, 5) are relaxed entirely by $V \rightarrow R$, T collisions, i.e. none of the calculated v = 1 rise due to high states is observed. Because of the simultaneous, slower relaxation of the lower v-states, this result has a fairly large uncertainty, i.e. we estimate 80 to 100% $V \rightarrow R$, T efficiency. Even more surprising is the fact that the lower (4, 3) states also show large $V \rightarrow R$, T channels, in the >50% probability range. This finding supports recent theoretical analysis by Billing and Poulsen for HF (J. Chem. Phys. $\underline{68}$, 5128 (1978)). Further work on this important problem is under way.

2. Electron Ion Recombination Under Laser Plasma Conditions (M. A. Biondi)

Owing to problems with very small amounts of nitrogen (few p. p. m.) in the neon the dissociative recombination studies in neon afterglows have been transferred to a longer-term research program on laser collision processes. Instead, we have proceeded with redesign of the microwave afterglow apparatus for studies of the recombination of electrons with metal halide ions, metal dimer ions, and metal-rare gas ions. The first systems to be investigated will be $HgCl^+$, Hg^+_2 and $Hg^+ \cdot Xe$. It is expected that apparatus modifications for these studies will be completed in the next report period.

3. Ion-Molecule (Two- and Three-Body) Charge Transfer Processes (M. A. Biondi)

The two-body reactions of He^+ and Ne^+ with Xe atoms have been studied for the modelling of excimer lasers using a light noble gas as majority constituent. At 300 K, the rate of the reaction

$$Ne^+ + Xe \rightarrow Ne + Xe^+ \; (+h\nu) \qquad (1)$$

is found to be $k_1 = (1.4 \pm 0.5) \times 10^{-14}$ cm^3/sec; that is, with no curve crossing accessible at the appropriate energies, the reaction proceeds via the very slow radiative charge transfer process. However, the corresponding reaction for helium

$$He^+ + Xe \rightarrow He + Xe^{+*} \qquad (2)$$

proceeds more rapidly, $k_2 = (4 \pm 1) \times 10^{-12}$ cm^3/sec at 300 K. In this case, suitable curve crossings leading to excited Xe^+ ions make the reaction more likely.

The three-body contributions to these reactions may be of considerable importance; however, their magnitudes have not yet been determined.

4. Dissociative Excitation of Molecules by Electron Impact (E. C. Zipf)

Work continues on the construction of a second generation Time-of-Flight [TOF] apparatus in which ion and neutral dissociation fragments can be detected simultaneously. The apparatus is designed so that associative ionization processes involving the kinetically and electronically energetic products can also be studied.

Our work on the dissociative excitation of metastable $N(^2D)$ and $N(^2P)$ atoms from electron bombardment of N_2 has been written up and submitted for publication. Similar papers on the dissociative excitation of O_2 and NH_3 are in preparation. Our double-monochromator electron-excitation apparatus is being modified now so that electron scattering studies of highly reactive species such as Cl, Fl, O, H, and N can be carried out over the wavelength range 500 $\overset{\circ}{A}$ - 1 micron.

5. Theoretical Calculations (J. N. Bardsley)

Since our last report, we have completed our computer program to perform Monte-Carlo calculations of the rates of ion-ion recombination in dense gases. The program has been checked by exploratory calculations on $Kr^+ + F^-$ and $Hg^+ + Cl^-$ in an argon diluent at pressures between 0.1 and 2 atmospheres.

The calculation of the recombination rate involves two steps. We first calculate analytically the rate at which the ions approach within a separation R_o using standard transport theory. The radius R_o must be sufficiently large that the interaction between the ions can be treated as a perturbation for $R > R_o$ and we can determine the flux and the velocity distribution of the approaching ion-pairs. Then we calculate the probability that the ions that approach within R_o undergo recombination. This second step involves the Monte-Carlo simulation which permits us to include an arbitrary description of the microscopic process. The recombination occurs because of the loss of kinetic energy to the neutral gas molecules and/or because of Landau-Zener-like transitions to two neutral atoms.

To the best of our knowledge the only other theorist involved in this type of work is Sir David Bates in Belfast. Because of other problems, Bates has not yet applied his program to any systems of laser interest, although his computer program was completed long before ours. In September, J. N. Bardsley was able to meet with Bates to discuss the differences between our codes. We were particularly concerned that the Belfast group might have considered the method that we chose to use and rejected it on some grounds. It appears that this is not the case, and that Bates was only aware of one technique for solving the problem when they wrote their code. We believe that our approach is more convenient and more efficient and will continue to use it in preference to theirs.

Our exploratory calculations have been designed to determine the best choice of the radius R_o, and to check that the results do not depend critically on the value of

R_o. We also have been attempting to improve the efficiency of the program, so that we can increase the number of production runs that we can perform within our computer allocation. We are confident that we will be able to study several systems over a range of temperatures and pressures with statistical errors that are significantly smaller than the uncertainty in the cross section data that is used as input to the code.

Our results have already shown that the classical Natanson theory can significantly underestimate the recombination rate at intermediate pressures. We have also confirmed the result of Bates and Medas that the low pressure regime was treated badly in the classical theories.

In performing these calculations we have discovered a generalization of a basic result in transport theory that was derived by Dirac in 1943. This result may have broad implications in transport theory in weakly absorbing media, and is being submitted to a mathematical journal.

B. Optics

1. Particulate Technology (W. L. Fite)

Activity over the past six months has concentrated on (1) continued measurements on doping of hot surfaces to produce ion pulses when pure water droplets and ice crystals strike them, and (2) measurements to correlate ion pulse heights with sizes of particulates of alkaline salts impacting on conventional surfaces under pressure and flow conditions simulating the stratosphere.

The progress on item (1) has been good. It is found that the pulses are slow, with typical pulse widths being in the millisecond range. This is in contrast to pulse widths of a few tens of microseconds for particulates with surface ionizable constituents striking conventional hot surfaces. Correlation of pulse heights and shapes with particle size (normally in the 10 to 50 micron diameter range) has

been fairly good, with the standard deviation for the total number of ions produced over the entire pulse being in the range of 20% of the mean pulse height. For droplets less than about 30 microns in diameter, the maximum height of the pulse appears to correlate well with particle size also. In both cases, however, the parameter value goes approximately as the 0.5 power of the diameter. This is a surprising result and indicates that the role of the droplet in initiating the reactions that release ions from the surface is far from that anticipated. It had been expected that the variation would be according to a power of diameter greater than 1. It is found that by operating the doped surfaces at high temperatures (of the order of 1100° C) the ions produced from the hot surfaces dominate ions produced by impurities in the droplet.

In the second activity, measurements have been made on the electrical pulse distributions generated when residues of salt solution droplets produced by a monodisperse aerosol generator strike a hot wire (platinum) detector at velocities in the parachute drop range and pressures in the stratospheric pressure range. It is found that there are always some low height pulses present, presumably from fragmentation of some of the particles on impact at the wire. However, the distribution does show a pronounced maximum under almost all conditions, with a full width at half maximum of the most probable pulse height from 25% at 1 micron diameters to 60% at 11 microns.

II. Publications and Technical Presentations

A. Publications

The Mobility of He^+ Ions in He, with Swati Sinha and S. L., and J. N. Bardsley, submitted for publication.

The Thermal Rate Constant of Elementary Reactions: Does Specificity of Energy Disposal Require a Concomitant Lowering of its Magnitude?, F. Kaufman and R. D. Levine, Chem. Phys. Letters, 54, 407 (1978).

Reply to Comment on Mechanism of NO_2 Fluorescence, V. M. Donnelly and F. Kaufman, J. Chem. Phys. 68, 5671 (1978).

Fluorescence Lifetime Studies of NO_2. II. Dependence of the Perturbed $^2B_2$ State Lifetimes on Excitation Energy, V. M. Donnelly and F. Kaufman, J. Chem. Phys. 69, 1456 (1978).

The Excitation and Collisional Deactivation of Metastable $N(^2P)$ Atoms in Auroras, E. C. Zipf, P. J. Espy, and C. F. Boyle, submitted to J. Geophys. Res., 1978.

B. Technical Presentations

Molecular Resonance Phenomena, a paper presented by J. N. Bardsley at the Workshop on Electron- and Photon-Molecule Collisions at Asilomar, California, on August 3, 1978.

Particulate Detection Using Surface Ionization, lecture given at the Morgantown Energy Research Center, Department of Energy, Morgantown, W. VA, August 17, 1978, by Wade L. Fite.

Kinetics of Thermal Atom and Radical Reactions. Experiment and Interpretation, invited paper given by F. Kaufman at 1978 Conference on the Dynamics of Molecular Collisions, Asilomar, CA, June 29, 1978.

Electron-Impact Dissociation of O_2: Excitation of the OI Quintet States, M. Gorman and E. C. Zipf, presented at G. E. C., October, 1978.

Metastable Fragmentation of NH_3 Induced by Electron Bombardment, B. L. Carnahan and E. C. Zipf, presented at G. E. C., October, 1978

C. Other Activities Relating to ARPA

J. N. Bardsley attended a conference on Computational Atomic and Molecular Physics at Nottingham, England, in September, 1978.

F. Kaufman attended a meeting of the NASA Advisory Committee on Upper Atmosphere Research in Washington, DC, on May 8 and 9, 1978.

F. Kaufman attended a meeting of the Advisory Committee of the Chemistry Division of the National Science Foundation in Washington, DC, on May 11 and 12, 1978.

F. Kaufman attended a meeting of the Reaction Rate Working Group of the Defense Nuclear Agency at the Naval Research Laboratory, Washington, DC, on May 24, 1978.

F. Kaufman was the organizer and general chairman of a Symposium on the Current Status of Kinetics of Elementary Gas Reactions at the National Bureau of Standards, Gaithersburg, MD, on June 19, 20, and 21, 1978.

F. Kaufman was elected Vice President of the Combustion Institute at its Board of Directors meeting at the 17th International Combustion Symposium at Leeds, England, August 20 - 25, 1978.

III. Visiting Scientists

Dr. B. D. Buckley, Daresbury Laboratory, England

W. Huntress, Jet Propulsion Laboratory

Herman Beyerinck, Eindhoven University of Technology

IV. Degrees Awarded

Jeffrey Halle, Ph.D., July, 1978.

Senior Investigator	Est. Funds Expended and Committed (Thous.)
J. N. Bardsley	84.4
M. A. Biondi	156.7
W. L. Fite	53.0
F. Kaufman	143.0
E. C. Zipf	42.9
Total Expended and Committed	480.0
Available Funds	515.0
Estimated Funds Remaining as of 9/30/78	35.0

University Accounting of Funds

Expended as of 9/30/78	476.5
Available Funds	515.0
Remaining Funds as of 9/30/78	38.5